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<b>13. ABSTRACT (Maximum 200 Words)</b>  This project consists of experiments and theoretical modeling designed to improve our understanding of the detailed chemical kinetics of supercritical water oxidation (SCWO) processes. The objective of the three year project is to develop working models that accurately predict the oxidation rates and mechanisms for a variety of key organic species over the range of temperatures and pressures important for industrial applications. Our examination of reaction kinetics in supercritical water undertakes <i>in situ</i> measurements of reactants, intermediates, and products using optical spectroscopic techniques, primarily Raman spectroscopy. Our focus is to measure the primary oxidation steps that occur in the oxidation of methanol, higher alcohols, methylene chloride, and some simple organic compounds containing nitro groups. We are placing special emphasis on identifying reaction steps that involve hydroxyl radical, hydroperoxyl radical, and hydrogen peroxide. The measurements are conducted in two optically accessible reactors, the supercritical flow reactor (SFR) and the supercritical cell reactor (SCR), designed to operate at temperatures and pressures up to 600°C and 500 MPa. The combination of these two reactors permit reaction rate measurements ranging from 0.1 s to many hours.				
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# Kinetics of Supercritical Water Oxidation

## SERDP Compliance Technical Thrust Area

### Quarterly Report

Sandia National Laboratories  
Combustion Research Facility  
Case 8610.000

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### Project description

This project consists of experiments and theoretical modeling designed to improve our understanding of the detailed chemical kinetics of supercritical water oxidation (SCWO) processes. The objective of the three-year project is to develop working models that accurately predict the oxidation rates and mechanisms for a variety of key organic species over the range of temperatures and pressures important for industrial applications. Our examination of reaction kinetics in supercritical water undertakes *in situ* measurements of reactants, intermediates, and products using optical spectroscopic techniques, primarily Raman spectroscopy. Our focus is to measure the primary oxidation steps that occur in the oxidation of methanol, higher alcohols, methylene chloride, and some simple organic compounds containing nitro groups. We are placing special emphasis on identifying reaction steps that involve hydroxyl radical, hydroperoxyl radical, and hydrogen peroxide. The measurements are conducted in two optically accessible reactors, the supercritical flow reactor (SFR) and the supercritical cell reactor (SCR), designed to operate at temperatures and pressures up to 600°C and 500 MPa. The combination of these two reactors permit reaction rate measurements ranging from 0.1 s to many hours.

The work conducted here continues the experimental approach from our previous SERDP-funded project by extending measurements on key oxidant species and

expanding the variety of experimental methods, primarily optical in nature, that can be used to examine reactions at SCWO conditions. Direct support will be sent to the project collaborators at MIT and Princeton who will contribute to model development for phenol and halogenated species. These researchers will examine these processes using more conventional sample and quench methods. The experiments at Sandia and at the universities all focus on determining the primary oxidation steps that involve the OH and HO<sub>2</sub> radicals, generating data that will be used to evaluate and refine SCWO reaction kinetic schemes. The primary technical difficulty in this stage of the project will be recasting existing high temperature (1100 °C) chemical kinetic models for these simple molecules to 400-600 °C. At these temperatures, the role of the HO<sub>2</sub> radical becomes important.

### *Executive Summary of Progress this Period*

#### **Programmatic**

The two most important programmatic events were the receipt of the SERDP FY95 \$300K funding and the submission of the SERDP FY96 Project Execution Plan for funding of \$460K. The receipt of the \$300K keeps the project on track with no interruption, and the expected receipt of \$460K in the first half of FY96 will permit us to initiate renewal for the two subcontracts with MIT and Princeton in a timely fashion to guarantee no interruption in those activities.

There were several personnel milestones that occurred. Åsa (Karlegård) Rydén completed her visit and returned to Lund, Sweden. Much of her work conducted January - June, 1995 will be incorporated into the modeling analysis paper we are preparing. The project was fortunate to have Christopher Griffith, an undergraduate student from Princeton University, visit and work on some of the modeling of methane. An arrangement has been worked out with Dr. Eric Croiset from CNRS Orleans (France) to work with us for a year starting in January 1996. He comes with considerable experience in the combustion field, as well as SCWO experience from having worked with Prof. M.J. Antal at the U. of Hawaii. He will be a valuable addition to the SCWO team. We have initiated a search for another postdoctoral associate to support the project, replacing Tom Hunter, who leaves in December, 1995 for a permanent position at 3M.

R.R. Steeper completed his Ph.D. thesis last quarter. His thesis is an important Milestone Report and will be available as a Sandia Report next quarter.

#### **Methane and methanol oxidation**

Work this quarter focused on interpreting the C<sub>1</sub> oxidation model that performed well for methanol. We applied the model to methane oxidation experimental data and compared its performance with other reaction chemistry models. The primary

issue to be resolved is the lack of reliable thermodynamic parameters and rate constants for the reactivity of  $\text{CH}_3\text{O}_2$ , the methylperoxyl radical. Older models ignore the potential existence of this species although it is critical in determining intermediate product formation in methane oxidation. It has an impact on the prediction of the rate dependence on oxygen concentration over a range of temperatures. A new  $\text{C}_1$  model developed by E.E. Brock in Prof. P.E. Savage's group at U. of Michigan <sup>1</sup> may clarify this issue and will be investigated next quarter.

However, we have recognized that the models that have been developed (Tester and co-workers <sup>2,3</sup>, Butler, Pitz and co-workers <sup>4,5</sup>, and Savage and co-workers <sup>1</sup>) are different combinations of a number of earlier combustion models. Some of these SCWO models are insufficiently documented and others are not well-tested for their extrapolation to combustion conditions. We think it is important to have well-established link between a SCWO elementary reaction model and combustion mechanisms. Recently, the Gas Research Institute (GRI) developed a well-documented and optimized model for the oxidation of methane that is appropriate for combustion applications <sup>6</sup>. As a result, it is probably now best to use this model as a starting point for a SCWO model that connects methanol and methane oxidation at SCWO conditions to higher temperature models.

During this quarter, a paper was completed and submitted to *Industrial and Engineering Chemistry Research* titled "Raman Spectroscopic Measurement of Oxidation in Supercritical Water I. Conversion of Methanol to Formaldehyde". The paper identifies several important differences between existing models for the oxidation of methanol and reveals that the model developed by the Pitz/Butler collaboration <sup>4,5</sup> best reproduced our experimental data. Also this quarter, the GRI reaction mechanism was first tested at SCWO conditions yielding induction times considerably longer than measured in our SFR. We suspect that the GRI mechanism underpredicts the reactivity of  $\text{HO}_2$  at lower temperatures and we surmise that an enhanced  $\text{HO}_2$  reactivity would significantly reduce the predicted induction time.

### Isopropanol oxidation

Most of the experimental work this quarter was aimed at isopropanol and n-propanol oxidation. In addition, a paper was submitted to *Industrial and Engineering Chemistry Research* titled "Raman Spectroscopic Measurement of Oxidation in Supercritical Water II. Conversion of Isopropanol to Acetone" based on our experimental data. We have identified that n-propanol reacts significantly faster than isopropanol in the 410 - 470 °C range. A stable intermediate species is formed during n-propanol oxidation, but it is more reactive than n-propanol itself. A modification of the SFR was completed to prevent the possibility of partial pyrolysis in the preheater that could affect the oxidation results.

## CO/CO<sub>2</sub> water-gas shift chemistry

During this quarter we began experiments on the simple water gas shift reaction,  $\text{CO} + \text{H}_2\text{O} \Rightarrow \text{H}_2 + \text{CO}_2$ , to examine the effect of water on the stability of transition states in supercritical water. Melius and Bergan <sup>7</sup> have predicted, based on *ab initio* calculations, that there should be a dramatic change in the apparent activation energy of this reaction due to the presence of excess water. Preliminary measurements show an increase in total rate with additional water concentration, which is due to the direct participation of water as a reactant, as would be expected. However, we have not yet accessed water densities sufficiently high to produce an increase in the rate constant.

## Future work

Work next quarter will focus on completing the propanol oxidation measurements in the SFR reactor. We will expand the data set on isopropanol, conduct experiments on n-propanol, and convert these measurements to a skeleton engineering model for oxidation of higher alcohols. Our present understanding of the initial step in isopropanol oxidation suggests that n-propanol may behave differently. We will coordinate lab availability to begin experiments on thermal decomposition of H<sub>2</sub>O<sub>2</sub>. As mentioned in previous reports, these experiments will provide a direct measurement of hydrogen peroxide dissociation rates in supercritical water. Our modeling effort will focus on linking the methane and methanol models to the GRI high-temperature model such that we have a self-consistent scheme with a traceable set of elementary reactions.

## Publications & presentations

S.F. Rice, T.B. Hunter, Å.C. Rydén, R.G. Hanush; "Raman Spectroscopic Measurement of Oxidation in Supercritical Water I. Conversion of Methanol to Formaldehyde." submitted to Industrial and Engineering Chemistry Research. 8/95.

T.B. Hunter, S.F. Rice, R.G. Hanush; "Raman Spectroscopic Measurement of Oxidation in Supercritical Water II. Conversion of Isopropanol to Acetone" submitted to Industrial and Engineering Chemistry Research. 8/95.

## *Detailed Summary of Technical Progress this Period*

### **Methane and methanol oxidation**

#### *Methane*

Sufficient data on methane and methanol oxidation in supercritical water has been generated from experiments at Sandia and elsewhere to permit the development of a single simplified kinetics mechanism to model these two species. To initiate this effort, we needed to choose a starting point mechanism with which to test the overall performance of the results. Our choice could be made from the "Webley" mechanism <sup>2,8</sup>, the Pitz/Butler set of mechanisms <sup>4,5</sup>, and the GRI high temperature methane combustion mechanism <sup>6</sup>.

Because methane and methanol are the simplest organic C<sub>1</sub> species, at first glance it might seem that mechanisms describing the oxidation of these two systems would be similar with extensive overlap of key reactions. This is not entirely true. Although oxidation of both of these species ultimately produces only CO<sub>2</sub> and water, the methanol system is significantly simpler. We initially thought that nearly all of the methane would pass through methanol as a reactive intermediate requiring only the addition of a methane-to-methanol conversion sub-mechanism to the successful methanol model. However, we found that the methane-to-methanol sub-mechanism opens up a pathway to formaldehyde (and subsequently CO<sub>2</sub>) that do not pass through methanol. The intermediate species common to the two systems is formaldehyde.

Figure 1 shows a reduced flux diagram for the oxidation of methane at 250 bar (3670 psia) and 500 °C. Only net fluxes are shown here, with the exception of the quasi-equilibrium of the  $\text{CH}_3 + \text{O}_2 = \text{CH}_3\text{O}_2$  addition reaction. The methanol oxidation reaction is a subset of the overall methane oxidation, but most of the methane does not pass through methanol. Most of it goes through the  $\text{CH}_3\text{O}$  radical and then on to formaldehyde,  $\text{CH}_2\text{O}$ . In fact, it is the reaction chemistry of the methylperoxyl radical  $\text{CH}_3\text{O}_2$ , analogous to the behavior of the peroxy radical ( $\text{HO}_2$ ) in the methanol system, that controls the irreversible oxidation steps involved in the conversion of methane to formaldehyde. A preliminary sensitivity analysis completed this quarter shows that the overall methane consumption rate is sensitive to all of the reactions that consume  $\text{CH}_3\text{O}_2$ . The main route to methanol is through the unusual reaction of  $\text{CH}_3\text{O}_2$  with itself to produce three products,  $\text{O}_2$ ,  $\text{CH}_2\text{O}$ , and  $\text{CH}_3\text{OH}$ .

The methanol-to-formaldehyde part of the mechanism reproduces our experimental results well over the 440 - 500 °C temperature range. Further experimental and theoretical work is needed to refine and verify the role of  $\text{CH}_3\text{O}_2$  in the scheme. Simultaneously, this scheme needs to be analyzed in greater detail to determine how well it reproduces the existing experimental results.

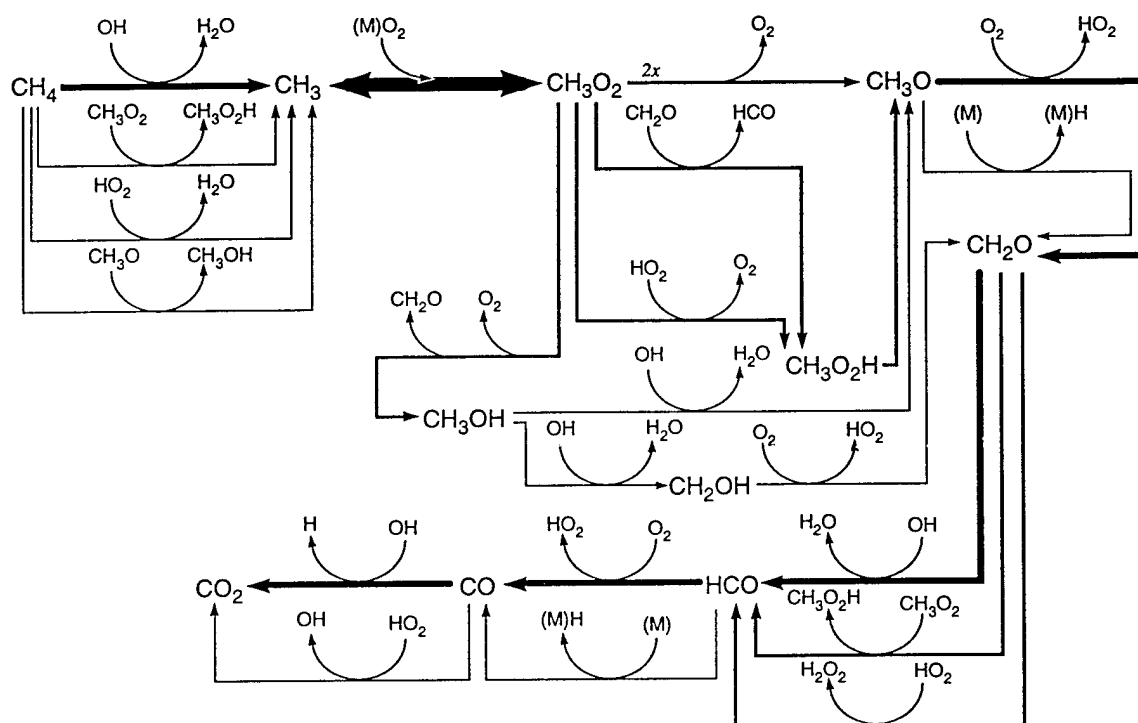


Figure 1. Flux diagram of the oxidation of methane at 500 °C and 250 bar in supercritical water. The four weightings of arrows roughly reflect the overall flux through each reaction step. This map represents the flux at approximately 50% conversion.

We have attempted to reconcile the two existing methane oxidation mechanisms, which we refer to as "Webley" and "Pitz". For the most part, the kinetic parameters in the Pitz mechanism are traceable to the references that are reported <sup>9-11</sup> and the thermodynamic information is from the Chemkin library <sup>12</sup>. The kinetic parameters in the Webley mechanism are also traceable as stated in Ref. 2. But because the reactions are written as equilibria, all the reverse reaction rates must be calculated from thermodynamic parameters referenced to the 1971 JANNAF tables. Unfortunately, several of the species, including methanol, are not in the 1971 tables. Thus, using the Webley mechanism unmodified is not possible. In addition, the Webley mechanism lacks the  $\text{CH}_3\text{O}_2$  species entirely and, as a result, produces fundamentally different methane oxidation predictions than the Pitz mechanism. With this in mind, we have chosen to abandon the Webley mechanism as an initial set of reactions and focus on the Pitz mechanism as a "low-temperature" starting point and the GRI mechanism as a well-documented, high-temperature system. In merging these two mechanism, it will be desirable to have as many steps as possible in common for the two mechanisms.

The GRI mechanism, since it was configured for higher temperatures, lacks many of the steps included in the Pitz mechanism. Especially critical in this regard, is the

absence of induction-period reactions for methanol, such as  $\text{CH}_3\text{OH} + \text{HO}_2 \Rightarrow \text{CH}_2\text{OH} + \text{H}_2\text{O}_2$ . Thus, the GRI mechanism is not well designed to handle temperatures pertinent to SCWO for methanol, but may prove to be adequate for methane.

Just as this quarter ended, another  $\text{C}_1$  mechanism was published by Brock and Savage <sup>1</sup> that attempts to achieve the same goal as our work. They compare their  $\text{C}_1$  mechanism to the available data for  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CH}_3\text{OH}$ , and  $\text{CH}_4$  oxidation results. Next quarter we will begin to include the Brock work in our model assessments.

### *Methanol*

The most important result this quarter was the completion of the paper "Raman Spectroscopic Measurement of Oxidation in Supercritical Water I. Conversion of Methanol to Formaldehyde." and submission to the journal *Industrial and Engineering Chemistry Research*. This paper documents most of the work that we have completed to date on methanol oxidation and includes a detailed description of our experimental, Raman-based, analytical method. However, in addition to the manuscript preparation, we have continued to develop a more complete picture of the differences between the several available elementary models. Most of our emphasis has been placed on identifying the "starting point" of the GRI 1.1 mechanism and examining the primary differences between it and the mechanism that Pitz, Butler, and co-workers developed in 1991 that successfully reproduces our experimental results <sup>5</sup>.

Figure 2 shows methanol oxidation predictions of the GRI mechanism at 500 °C along with data from our experiments. The GRI model fails to properly reproduce the experimental data. It has a much larger induction period because it omits two key reactions,  $\text{CH}_3\text{OH} + \text{HO}_2 \Rightarrow \text{CH}_2\text{OH} + \text{H}_2\text{O}_2$  and  $\text{CH}_3\text{OH} + \text{O}_2 \Rightarrow \text{CH}_2\text{OH} + \text{HO}_2$ . If these are included in the GRI mechanism, using parameter values from the Pitz mechanism, good agreement is obtained. These two key low-temperature steps critically affect the length of the induction period, but only moderately affect the rate of the bulk of the reaction.



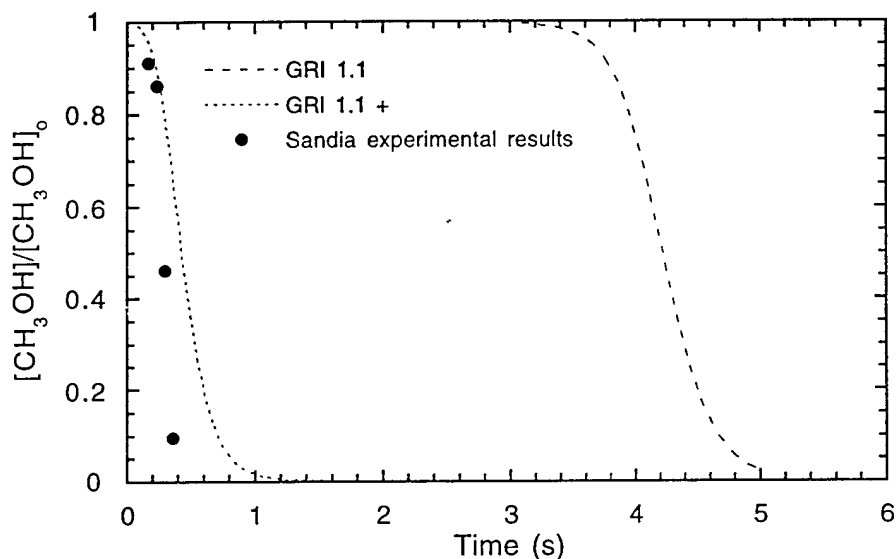


Figure 2. Comparison of the results from the GRI 1.1 mechanism for the oxidation of methanol at 25.0 MPa and 500 °C.  $[\text{CH}_3\text{OH}]/[\text{CH}_3\text{OH}]_0$  refers to the concentration of methanol measured divided by the initial feed concentration. The curve marked GRI 1.1 is the prediction of the mechanism with no additions. The curve marked GRI 1.1+ has two reactions added,  $\text{CH}_3\text{OH} + \text{HO}_2 \Rightarrow \text{CH}_2\text{OH} + \text{H}_2\text{O}_2$  and  $\text{CH}_3\text{OH} + \text{O}_2 \Rightarrow \text{CH}_2\text{OH} + \text{HO}_2$  with kinetic parameters taken from the "Pitz" mechanism.

### Isopropanol oxidation

Our initial results on the kinetics and reaction pathways for oxidation of isopropanol were submitted for publication this quarter. Because of the appreciable formation of acetone that was measured, we have elected to examine how the oxidation of n-propanol may be different. Since n-propanol is unlikely to form acetone as an initial stable intermediate (as does isopropanol), we hypothesize that it should be less reactive. We suspect that the corresponding species to acetone, propionaldehyde, would probably not be easily formed, and as a result, the overall consumption of n-propanol should be slower than isopropanol at comparable conditions.

During this quarter, we made an important modification to the SFR fuel-feed method. We recognized that the lengthy fuel-preheating was causing some hydrolysis of the isopropanol at temperatures in excess of 450 °C prior to the

addition of the oxidizer. To rectify this problem, we modified the apparatus to permit injection of high concentration feed (using a high pressure liquid chromatography (HPLC) pump) just before the oxidizer mixing point. This modification also significantly simplifies operating procedures and prepares us for experiments planned for FY96. Some of these future tests support an ARPA-sponsored project at Sandia for the treatment of U.S. Navy excess hazardous materials and provide important leverage for this SERDP project.

This quarter, preliminary data on the oxidation kinetics of n-propanol in supercritical water were obtained with the SFR. Figure 3 shows a portion of the Raman spectrum of n-propanol in the 750 - 950  $\text{cm}^{-1}$  region. While the Raman feature at 845  $\text{cm}^{-1}$  overlaps the small peak at 880  $\text{cm}^{-1}$ , also due to n-propanol, it is nevertheless suitable for use as a measurement of n-propanol concentration. Figure 4 shows a spectrum of the reacting mixture of 0.16 mole/l  $\text{O}_2$  with 0.085 mole/l n-propanol at 430  $^{\circ}\text{C}$  and 250 bar after about 1 s of reaction. The Raman line at 845  $\text{cm}^{-1}$  of n-propanol is now blended with a new feature at 856  $\text{cm}^{-1}$  due to an intermediate. We have developed a fitting routine that allows us to separate the intensity contributions from n-propanol and this new species. At present, we have not been able to identify the species giving rise to this Raman line. Both ethanol and ethylene glycol are good candidates.

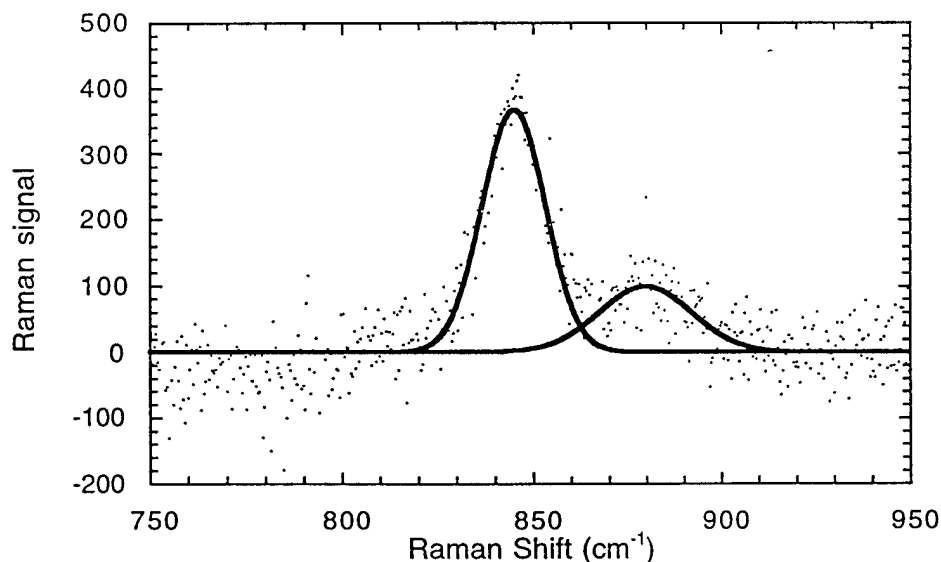


Figure 3. Typical spectrum of n-propanol in the 750 - 950  $\text{cm}^{-1}$  region. A spectral line fitting routine is used to aid in data reduction to determine total integrated intensities. The solid curves shown in the figure are the result of the curve fitting routine.

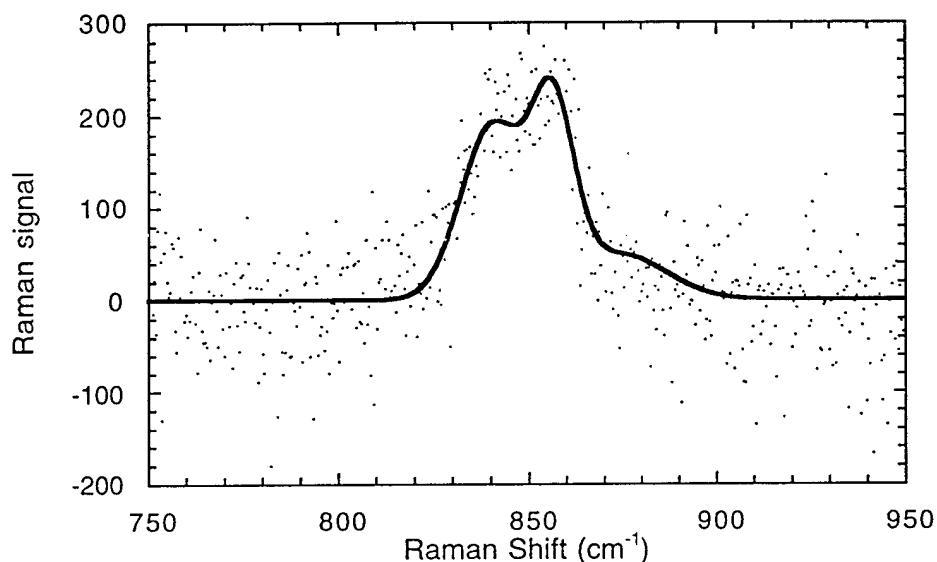


Figure 4: Typical spectrum of n-propanol in the 750 - 950  $\text{cm}^{-1}$  region after partial oxidation has occurred. The new feature at 856  $\text{cm}^{-1}$  is due to a stable reaction intermediate. The solid line is the sum of a fit to the known n-propanol spectrum (Figure 3) and the new line at 856  $\text{cm}^{-1}$ .

Our data show that, contrary to our initial suspicions, n-propanol is actually much more reactive than isopropanol. Not only does n-propanol disappear more rapidly under comparable conditions, but the production of CO and  $\text{CO}_2$  is also much faster. The rate of heat release during oxidation of n-propanol is significantly faster than that for isopropanol under identical conditions. It appears that the intermediate that is formed from the oxidation of n-propanol is less stable than acetone and rapidly reacts to form CO. At present we have not identified this intermediate, but expect to do so in the near future.

#### CO/ $\text{CO}_2$ water-gas shift chemistry

An important part of the overall understanding of the oxidation of any species in supercritical water is the role of the water molecule in the reacting system. There are several ways that water can affect oxidation rates in supercritical water. First, water is an explicit reactant in many elementary reactions, so that rates of these reactions are directly dependent on water concentration. Second, water is the most important collision partner for unimolecular reactions in the SCWO environment.

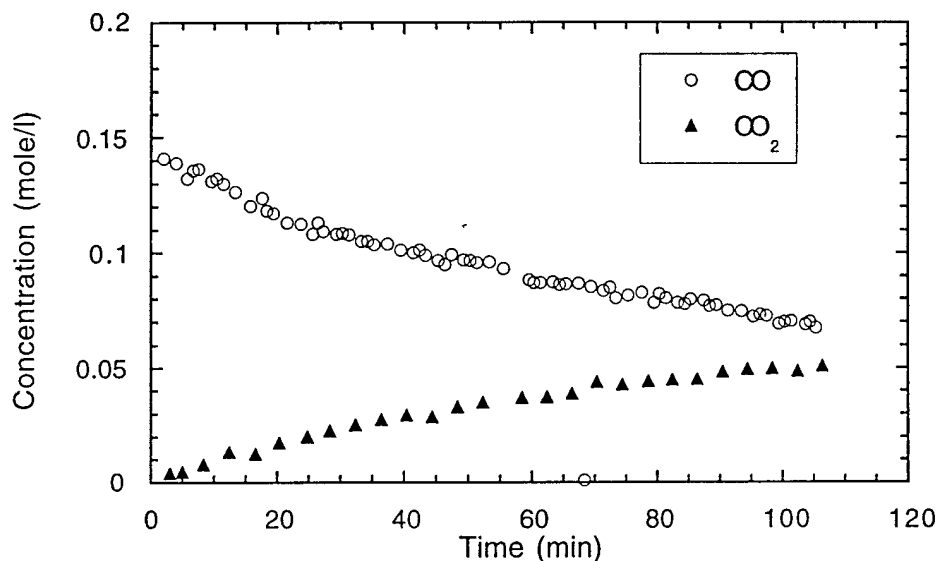


Figure 5. The reaction of CO in supercritical water at 450°C and 14.1 MPa. In the course of these experiments the production of H<sub>2</sub> is also monitored. The mass balance is not perfect, which is probably due to difficulties in obtaining reliable calibration of the CO Raman scattering cross-section.

Table 1  
Water Gas Shift Results:  $d[\text{CO}]/dt = -k_2 [\text{CO}] [\text{H}_2\text{O}]$  <sup>a</sup>

$-d[\text{CO}]/dt$ (mole/l-s)	$[\text{CO}]$ (mole/l)	$[\text{H}_2\text{O}]$ (mole/l)	Pressure (MPa)	$k_2$ (l/mole-s)
$2.92 \times 10^{-5}$	0.075	7.10	27.4	5.48
$2.36 \times 10^{-5}$	0.15	2.62	14.1	6.01
$2.50 \times 10^{-5}$	0.25	1.56	9.9	6.41

a - rate is evaluated at the initial CO reaction conditions

### Plans for next quarter

Emphasis will be placed on completing the experimental data set for n-propanol oxidation along with quantifying the rate of formation of CO and CO<sub>2</sub> in this system. We will also examine the rate of consumption of O<sub>2</sub>. This will be combined with the isopropanol results from earlier in the year. When this information is combined, we will be able to estimate the rate of heat release for both species. This is

critical engineering design information needed to evaluate the practicality of using isopropanol as a support fuel in SCWO reactors.

Our other main goal is to integrate the methane oxidation model with the methanol model that we have used up to this point and reconcile the integrated model with a high pressure version of the well-documented GRI mechanism. We will then use this  $C_1$  system as a basis for development of the fundamental mechanism for the oxidation of larger organic molecules. We will also explore the new mechanism proposed by Brock and Savage and compare it to our results on methane and methanol that as yet have not been available to Savage's group.

Water gas shift experiments will continue, but probably will not be completed next quarter. We will begin an analysis of our understanding of the equation of state for this four-species system to examine the effect of high water density on the energetics of the  $CO/CO_2$  equilibrium.

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